Semiclassical calculation of eigenvalues for higher order resonances in nonseparable oscillator systems

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It is shown how the "trajectory-close method" introduced in earlier papers of this series can be used to treat other resonant systems semiclassically. The method, which does not involve the use of any curvilinear coordinate system, is illustrated for two coupled oscillators which have 3:1, 4:1, 5:1, 3:2, and 5:2 internal resonances. It is readily executed and it is shown how it can be extended to the three-oscillator case. This work supplements our earlier studies of 1:1, 2:1, and 3:1 resonant systems using this technique. Shapes of eigentrajectories and of corresponding quantum mechanical wave functions are compared for each of these systems. The paper also contains a survey of and comparison with other semiclassical methods which have been applied to systems with internal resonances.

I. INTRODUCTION

A variety of methods have been used for the semiclassical treatment of molecular systems having classical resonances.[1–15] Such methods tend to complement quantum mechanical perturbation and variational treatments as well as each other. In the present article, we show how a trajectory method[16] which we termed the "trajectory-close method" and applied to 1:1, 2:1, and 3:1 resonances[3,5,14] can be used to treat in a simple way arbitrary classical resonances. The treatment is "exact" within the Einstein–Brillouin–Kramers or, as it is sometimes called, "primitive" semiclassical approximation. As before,[3,5,14] no special coordinate system is needed or used. It requires that the trajectories be quasiperiodic. The method is illustrated here using 3:1, 3:2, 5:2, 4:1, and 5:1 resonances for two-coordinate (2D) systems, thereby supplementing our earlier studies[3,5] of 1:1 and 2:1 resonances and of a 3:1 resonant avoided crossing problem.[14] The resulting eigenvalues and eigentrajectories are compared with their quantum mechanical counterparts. The method is readily extended to three-coordinate (3D) systems using a recently developed rapid calculation of zero-width Poincaré surfaces of section for three-dimensional systems.[17]

A second method which we introduced in Refs. 3 and 5 was based on the use of coordinate systems topologically appropriate to the shape of the trajectory.[3,18] With such coordinates one can, at least in some instances, introduce a uniform semiclassical approximation,[7,18] when it is needed for quantization of a particular state. However, almost all current methods for semiclassical quantization, including the present one, are based, instead, on the primitive semiclassical approximation.

The existence of the resonances themselves can be detected from the power spectrum of the trajectory.[19] For an (n,m) resonance, there will be two fundamental frequencies in the ratio $n:m$ and, in addition, the fundamentals show splittings (or side bands) due to the resonant coupling. The resonances can also be detected from the distorted "shape" of the trajectory, e.g., as in Refs. 1, 3, and 5 for 2D systems and Ref. 20 for 3D systems.

The method[3,5,14,16] is described in some detail in Sec. II. The results are given in Sec. III and discussed in Sec. IV. The various semiclassical methods for resonances are also considered there and comparisons are made. In particular, the trajectory-close method does not involve the use of curvilinear coordinate systems to treat resonant systems, unlike a number of other methods considered later. The preoccupation with such coordinate systems in Refs. 3 and 5 may have given a contrary impression.[8,21] In common with the other semiclassical methods, some knowledge of the distorted shape of the trajectory of the resonant system in coordinate space is needed. Even in a variational basis set quantum mechanical calculation of eigenvalues a knowledge of the shape of the wave function can reduce the number of basis set elements required for an accurate calculation.

II. METHOD

In an N-coordinate system, there are N topologically independent phase integrals $\oint p\,dq$. In the trajectory-close method, the total phase integral for one cycle of the trajectory is chosen as one of them. The ends of the trajectory are joined, for this purpose, on a cross section of the somewhat tube-like trajectory which occurs in the resonant system. A second (in the case of $N = 2$) independent phase integral is determined from the phase integral for the cross section of the tube-like trajectory, using a surface of section method.[14] With increasing numbers n and m in an $n:m$ resonance, the folds in the tube increase, but the present method is simply applied nevertheless.

A description of the method, which is given initially for the two-coordinate case follows next. The characteristics of the method are its simplicity, ease of execution, and straightforwardness.

The initial conditions for any 2D trajectory involves

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four quantities. One of these can be chosen to be the energy E. In the case of the present n:1 resonances arising from Eq. (4) given later the fraction $f_x = p_x^2/(p_x^2 + p_y^2)$ is specified, where the p's denote initial momenta, and the initial values of x and y are set equal to zero. In the case of the n:2 resonances the initial values of E and y are assigned and those of x and p_y are set equal zero. For a suitable initial choice for the value of E the unperturbed Hamiltonian sufficed.

The trajectory was then integrated using the DEROOT routine.[22] This routine both integrates the trajectory and, creating a remarkable simplification, automatically determine points on it which are roots of an equation provided by the user. In the present case we set the root-finding part of DEROOT to save points when the equation $y = 0$ was satisfied for an n:1 resonance and $x = 0$ for an n:2 resonance. These are the points on two surfaces of section and each set was next expressed in terms of values of the zeroth order action-angle variables (J and w, respectively) and then sorted, with a simple pairwise comparison program, in order of increasing w in the (0,1) interval for w. The area of the relevant $\oint J\,dw$ integral was calculated by a standard routine.[23] For the quantization the integral is then set equal to the right-hand side of Eq. (5) below.

A second action variable, the total action, was obtained as follows: When Hamilton's equations of motion were integrated to yield the classical trajectory the values of the action S along the trajectory were obtained at the same time by integrating an auxiliary equation

$$\frac{dS}{dt} = p_x\dot{x} + p_y\dot{y}. \tag{1}$$

After integration of only one cycle in a resonant system the trajectory returned almost to its starting point on the surface of section and the trapezoid rule sufficed to determine that portion of the total action J_T along the surface of section. (In nonresonant systems, not treated here, one or usually not more than several cycles sufficed to make the ends of the trajectory sufficiently close.) We then have for the value of J_T,

$$J_T = S + \tfrac{1}{2}(p_i + p_i^0)(q_i - q_i^0), \tag{2}$$

where q_i is x for the n:1 resonance and y for the n:2 resonance, q_i^0 is its initial value, p_i the momentum conjugate to q_i, and p_i^0 its initial value. For the quantization J_T is then set equal to the right-hand side of Eq. (6) below.

In the present procedure only three trajectories were needed for each eigenvalue (or less, in the modification described later): as initial values for E and χ we used the following initial pairs, χ denoting f_x in the n:1 case and y in the n:2 case: (E_1,χ_1), (E_2,χ_2), (E_2,χ_1). The values of n_i and N were then used to determine the a's, b's, and c's in the linear interpolation formula

$$\begin{aligned} n_i &= a_1E + b_1\chi + c_1, \\ N &= a_2E + b_2\chi + c_2, \end{aligned} \tag{3}$$

which was then used to determine the E which gave rise to integer values for n_i and N.

Two useful and accurate extensions[17,24] of the above method have recently become available. In one of these[24] the eigenvalues for a number of states are determined simultaneously, and the process required on the average only one trajectory per eigenvalue instead of the three needed in the present procedure: From a grid of points $n_i(E,\chi)$ and $N(E,\chi)$ Sheppard's method[25] is used to construct a surface for each of these functions using relatively few trajectories (points). From this surface E's are immediately obtainable for integer n_i's and N's.[24] Moreover, by using a grid of points there is also no need to guess at an initial E using, say, first-order perturbation theory.

A second simple extension of the present method is to three dimensions. In this extension a "zero-width" surface of section is obtained[17] from a 3D trajectory of only 200–300 periods. (In contrast, in an application of the adiabatic switching method to a 3D system[12(a)] 25 trajectories of about 100 periods each were used in the averaging process.) With this zero-width method one can determine a suface of section for (in the case of an x-cross section) J_x vs w_x, at a constant w_y and w_z and from it the integral $\oint J_x\,dw_x$ can be calculated. (The J's and w's again denote action-angle variables defined for the unperturbed integrable Hamiltonian.) Similar remarks apply to a J_y vs w_y surface of section at constant w_x and w_y (or to the J_z vs w_z one.) In a three-dimensional system, the cross-sectional line used for Eq. (2) becomes a cross-sectional plane, and there are now two, rather than one, such cross-sectional phase integrals used. The total phase integral in Eq. (6) is evaluated over one cycle of the trajectory as before. In practice several cycles of a trajectory are needed in the 3D resonant case to return to a point close to the initial one.

Perhaps surprisingly, the zero-width surface of section method,[17] in which a multidimensional interpolation is used, requires only a small Fortran program and little computer time.[17] The analog of Eq. (3), now for two n_i's and for N, is then used to obtain the eigenvalue. Once again, the number of trajectories (now four per eigenvalue in this 3D case) can be further reduced by applying the method in Ref. 24.

III. CALCULATIONS

The Hamiltonian used for the present illustration for n:m resonances is

$$\begin{aligned} H = {} & \tfrac{1}{2}(p_x^2 + p_y^2 + \omega_x^2x^2 + \omega_y^2y^2) \\ & - a(x^3 + y^3) + bx^my^n + cx^2y^2, \end{aligned} \tag{4}$$

where m and n are integers. This Hamiltonian was chosen because its simplicity permits an accurate quantum mechanical variational calculation of the eigenvalues needed for the comparison. (The semiclassical trajectory-based method is readily used, on the other hand, with much more complicated Hamiltonians.[26]) In a resonance having $\omega_x = n, \omega_y = m$, the resonant coupling term is bx^my^n. Examples of the trajectories for these systems are given in Figs. 1–5, which also serve to identify the difficulty in finding a practical analytical coordinate system for these cases were it needed.[18(b)] The cross-sectional line used for joining the two ends of a cycle of the trajectory as well as for calculating an independent phase integral is given below. The phase integral for this cross section is (in units of $\hbar = 1$)

$$\oint p_i\,dq_i = 2\pi(n_i + \tfrac{1}{2}). \tag{5}$$

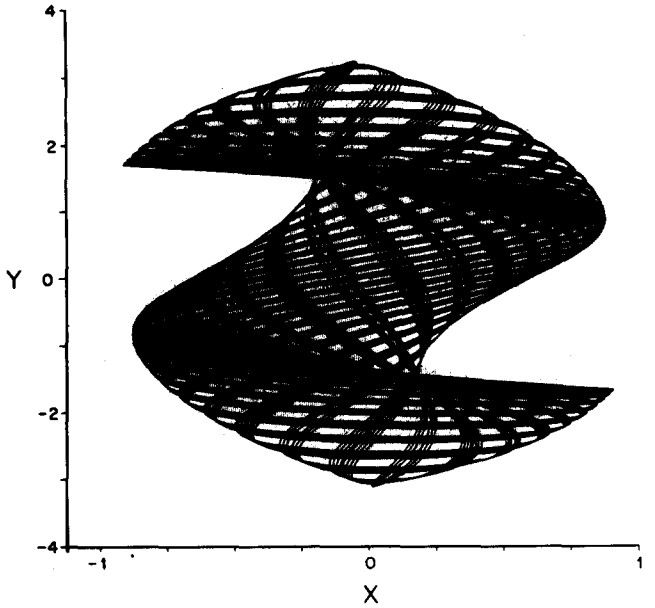

FIG. 1. 3:1 resonant classical trajectory for state $(3,0^-)$ in Table I. Parameters used were $\omega_x = 3$, $\omega_y = 1$, $a = 0.005$, $b = 0.05$, and $c = 0.01$.

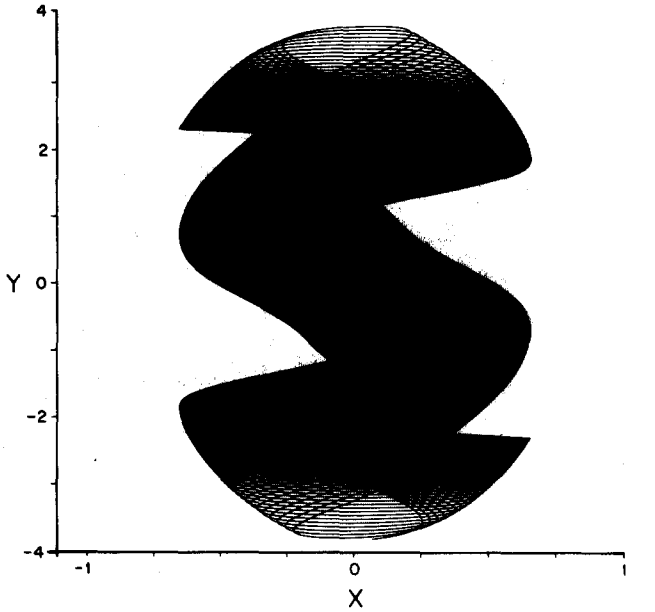

FIG. 3. 5:1 resonant classical trajectory for state $(5,0^-)$ in Table I. Parameters used were $\omega_x = 5$, $\omega_y = 1$, $a = c = 0.0001$, and $b = 0.001$.

For an eigentrajectory, n_i is an integer. The total phase integral along one cycle of the trajectory, the ends joined, is given by

$$\oint \sum_i p_i \, dq_i = 2\pi N + (n+m)\pi, \tag{6}$$

where N, an integer, is the principal quantum number for the state, and the $(n+m)\pi$ term arises because the trajectory touches its caustics $2(n+m)$ times during one cycle. There is a loss of phase $\pi/2$ each time, which must be included in semiclassical quantization, as in Eq. (6). As already noted in Sec. II the phase integral on the left-hand side of Eq. (6) includes a portion from joining the ends of the trajectory on the line used for the integral in Eq. (5). For n:1 resonances, the Poincaré surface of section chosen for Eq. (5) was $y = 0$ and consisted of one ellipse. For the n:2 resonances, the surface of section chosen was that for $x = 0$. There were n islands in this n:2 resonance, each of the same area. The area evaluated for Eq. (5) was for the island indicated in the figure captions (Figs. 4 and 5). The phase integral for Eq. (5) was, as already noted, computed in terms of action-angle variables rather than of ordinary coordinates and momenta.[27]

The states considered in Figs. 1–5 each occur in pairs, only one member of each pair being shown. They are the lowest zeroth-order degenerate pairs in each case, and so each figure represents only one state of the pair. The other state is approximately the y reflection for the n:1 resonance and the x reflection for the n:2 resonances. With increasing energy, some of the higher pairs became multifold degenerate in zeroth order, because of the increased number of ways of selecting pairs of integers (n_x, n_y) such that their weighted sum $n_x n + n_y m$ equals the integer N. A simple pattern

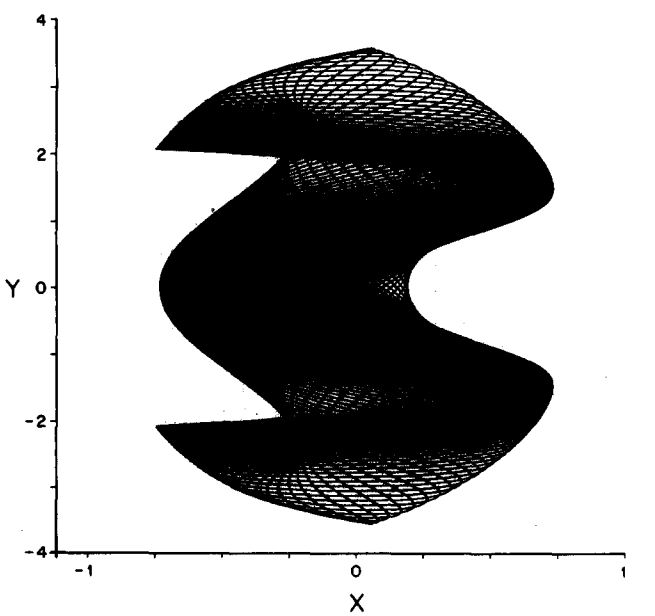

FIG. 2. 4:1 resonant classical trajectory for state $(4,0^-)$ in Table I. Parameters used were $\omega_x = 4$, $\omega_y = 1$, $a = c = 0.001$, and $b = 0.01$.

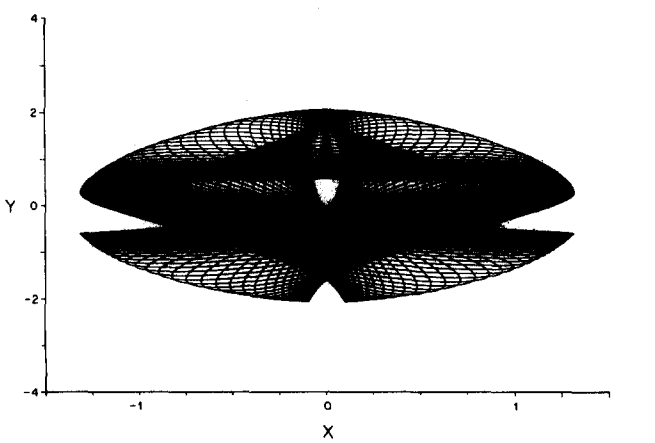

FIG. 4. 3:2 resonant classical trajectory for state $(6,0^-)$ in Table I. Parameters used were $\omega_x = 3$, $\omega_y = 2$, $a = 0.005$, $b = 0.08$, and $c = 0.01$. The surface of section used for Eq. (5) was on the line $x = 0$ and constituted the island between $y \sim 0.6$ and $y \sim 2$.

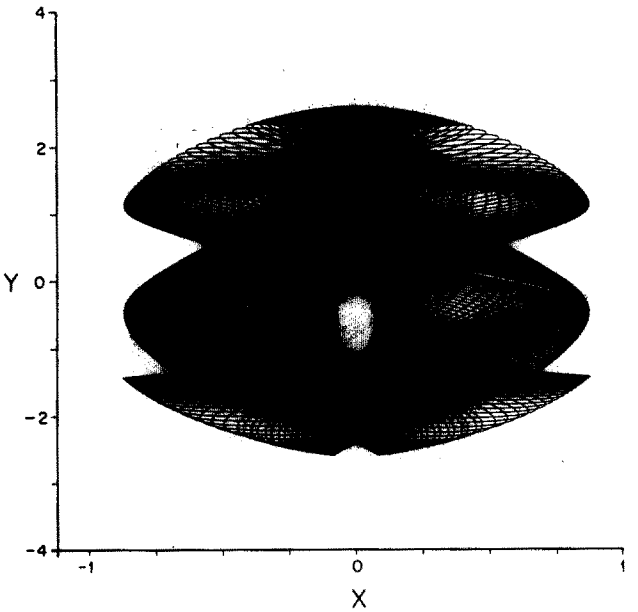

FIG. 5. 5:2 resonant classical trajectory for state $(10,0^-)$ in Table I. Parameters used were $\omega_x = 5$, $\omega_y = 2$, $a = 0.005$, $b = 0.04$, and $c = 0.007$. The surface of section used for Eq. (5) was on the line $x = 0$ and constituted the island between $y \sim 1.4$ and $y \sim 2.5$.

emerges for the degeneracy of such states in the n:1 case: n singly degenerate levels are followed by n doubly degenerate levels, then n triply degenerates levels, etc. For n:2 resonances the pattern is more complex. For example, in the 3:2 case, the sequence of degeneracies is 1, then 1 four times, 2,1, then 2 four times, 3, 2, then 3 four times, etc.

The plots of $|\Psi|^2$ for the states given in the previous figures are given in Figs. 6–10. A comparison with the plots for the trajectory shapes reveals their parallelism. Omitted in the present paper are plots of the surfaces of section, since they are similar to those given previously [p vs q in Ref. 2(c) and J vs w in Ref. 27]. The shapes of the trajectories suffice for our purposes to provide the desired topological information and, as seen later, are particularly useful for the other methods as well.

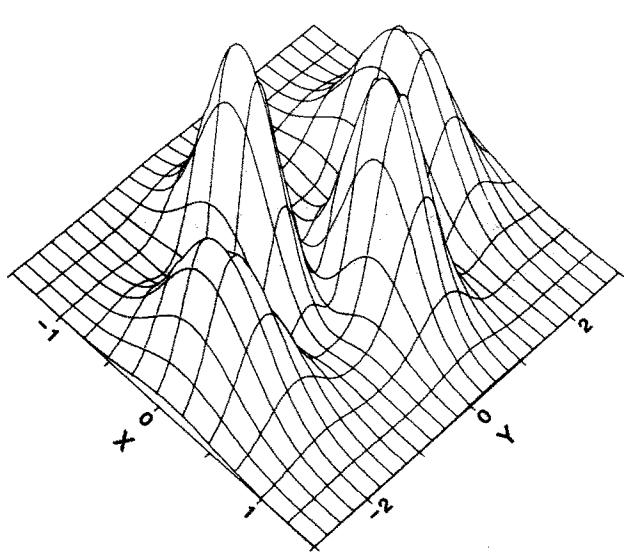

FIG. 6. $|\psi^2|$ for state $(3,0^-)$ in Table I.

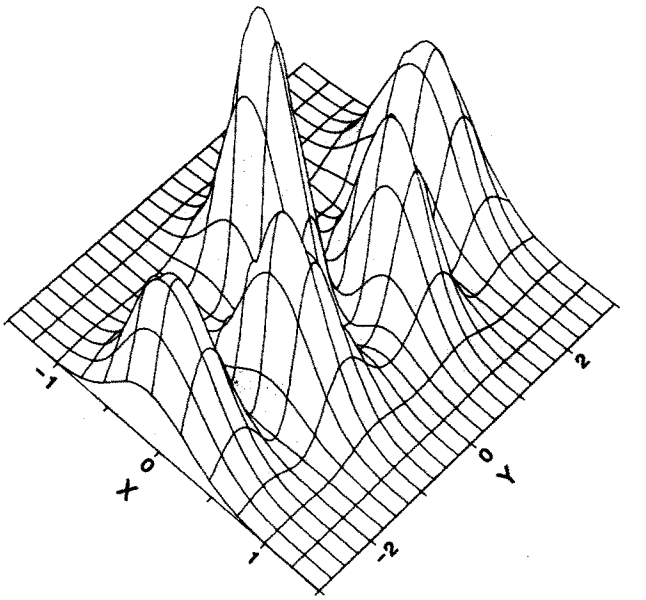

FIG. 7. $|\psi^2|$ for state $(4,0^-)$ in Table I.

IV. DISCUSSION

The agreement in Table I with the quantum mechanical eigenvalues is in each case seen to be very good. All of these states were doubly degenerate in zeroth order. Not shown are the states of lower energy, each of which is nondegenerate. Like the $l = 0$ states for a 1:1 case[2] and the $K = 0$ states (we realize now) for a 2:1 case[5] their semiclassical treatment would require either a uniform semiclassical (USC) quantization or the equivalent, perhaps, of a presently *ad hoc* Langer-type correction used in Ref. 12(b) for the $l = 0$ states of the 1:1 resonance.[12(b)] More generally, USC is needed whenever the trajectory involved is close to a separatrix of the motion (separating two types of motion), e.g., Ref. 15.[28]

We consider next,for comparison, several other methods actually used to calculate semiclassical eigenvalues in

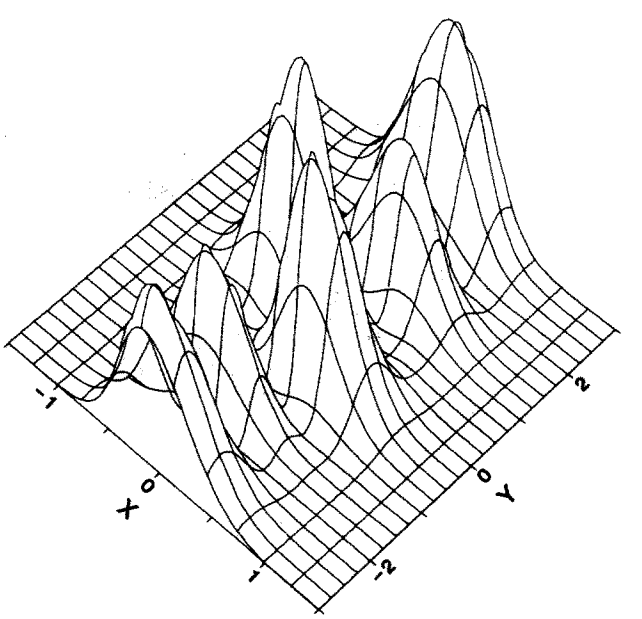

FIG. 8. $|\psi^2|$ for state $(5,0^-)$ in Table I.

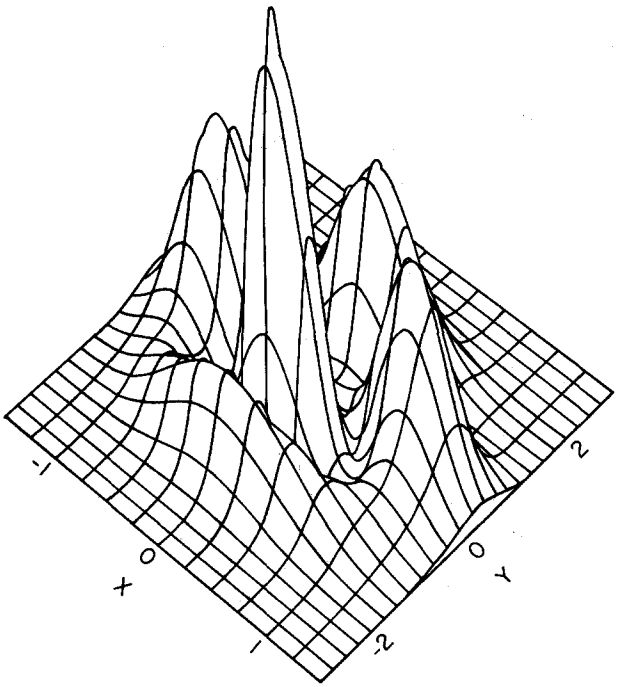

FIG. 9. $|\psi^2|$ for state $(6,0^-)$ in Table I.

resonance systems. We begin with the trajectory methods.

One such method is the Sorbie–Handy method.[2] In this method coordinate axes are chosen so that they intersect opposite caustics. When the shape of the trajectory is distorted sufficiently by a resonance, Cartesian coordinates become inadequate and curvilinear coordinates are then used.[2(a)] The method was successfully used for a resonance system in Ref. 2. Recently problems have been reported in Ref. 29, but

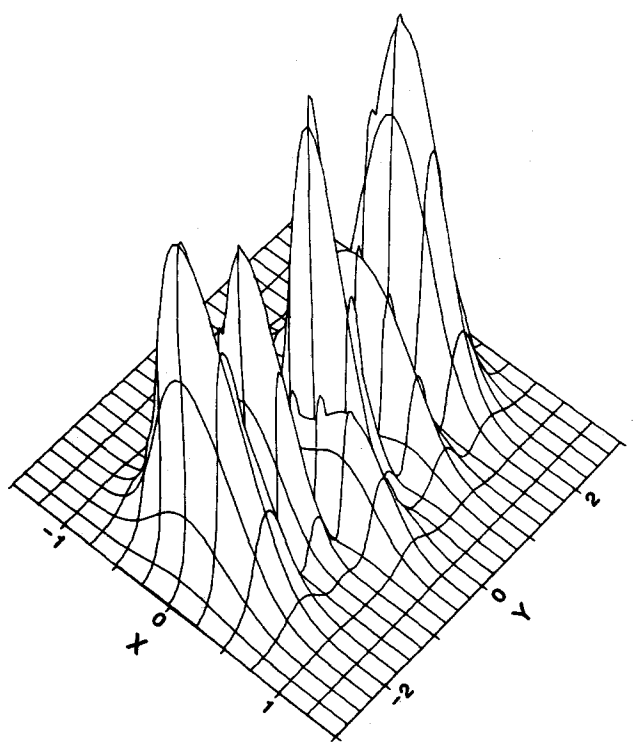

FIG. 10. $|\psi^2|$ for state $(10,0^-)$ in Table I.

TABLE I. Quantum and semiclassical eigenvalues.

Resonance (n,m)	State[a] (N_2,n_i)	State[b] (order)	E_q	E_{sc}	Figures[c] traj., quan.
(3,1)	$(3,0^-)$	4	4.977	4.976	1,6
	$(3,0^+)$	5	5.015	5.009	
(4,1)	$(4,0^-)$	5	6.494	6.492	2,7
	$(4,0^+)$	6	6.503	6.502	
(5,1)	$(5,0^-)$	6	7.999	7.999	3,8
	$(5,0^+)$	7	8.000	8.001	
(3,2)	$(6,0^-)$	6	8.499	8.500	4,9
	$(6,0^+)$	7	8.506	8.505	
(5,2)	$(10,0^-)$	9	13.494	13.499	5,10
	$(10,0^+)$	10	13.501	13.501	

[a] The minus denotes the member of the degenerate pair with lower energy.
[b] The states are ordered by energy, the lowest state being the ground state, and all states lower in order than the cited ones being nondegenerate.
[c] Figures 1–5 also give the parameters used in the Hamiltonian in Eq. (4).

no plots of the trajectories were given there, and so it is difficult to ascertain the source of the difficulty. The method itself tacitly uses an approximation described in an analysis of it in Ref. 3.

The first Fourier transform method was introduced by Noid *et al.*[19] for the purpose of calculating spacings of eigenvalues (infrared spectra),[19] for intensities of the spectral lines,[19] and for detecting classical chaos.[19] The method has been widely used for one or other of these purposes. Good agreement with quantum mechanical eigenvalue spacings and intensities has been found for nonresonant systems. In the case of resonant systems good agreement was found when the two eigenstates for the given spectral transition had wave functions (or trajectory plots) of the same shape.[19(b)]

Later, a Fourier transform method was used to calculate the individual eigenvalues themselves, both without[8,11] and with[9,11(a)] the use of the SH method. We denote these two methods by FT and FT–SH, respectively. FT–calculated eigenvalues have been obtained for a 1:1 resonance[8,11] and a 2:1 resonance.[8] In Ref. 11 curvilinear coordinates were introduced appropriate to the shape of the trajectory. A 1:1 resonance was treated in Ref. 11(a) for a 2D case, and many more eigenvalues were obtained with FT–SH and with the present trajectory-close method than with FT. Eigenvalues for all three methods, however, agreed with each other. The FT–SH method was reported to yield eigenvalues less sensitive to the spectral frequencies than were those obtained by FT.[11] Of the two methods FT–SH was indeed the one used by some of those authors.[9] To overcome these "stability" problems of FT, a "window" technique has been introduced to disentangle the determination of the frequencies and the amplitudes.[21]

Spectral methods can be very convenient. They also have some shortcomings: They require long-time trajectories to resolve the spectral frequencies when the latter are closely spaced (a problem avoidable with the present method).[30] In a resonance system peaks are split and can have side peaks. In one instance, to "resolve" two peaks, the system was deliberately perturbed to be off-resonant and an interpolation was then used.[21] A second problem with any

spectral method arises, of course, when the spectrum is complicated. As we ourselves noticed, there is then the problem of identifying the many individual spectral lines.

A newer proposed FT method is one which uses only a single trajectory and first order perturbation theory.[10,13] It has been applied to an electronic–vibrational problem.[31] (In the absence of trajectory plots it is not clear whether this problem is a resonance case. It probably is.) A USC method would have been needed to obtain good agreement for the problem. In a second application to a resonance system difficulties were reported,[32] but in the absence of trajectory shapes their origin is not clear. With the use of first order perturbation theory and a single trajectory one must choose actions for the single trajectory which are near enough the desired actions.[31]

The "adiabatic switching" method (AS)[4,12] appears to be a good one for calculating eigenvalues when resonances are absent from the Hamiltonian H and when at the same time they are either absent or not "strong" along the adiabatic path from the initial (unperturbed) H_0 to H. The method has been also used for a 1:1 resonance[4,12(a),12(b)] and for a 2:1 resonance,[12(c)] with encouraging results, usually making use of coordinates appropriate to the shape of the trajectories.[4,12] To use the method for such resonance systems a presently *ad hoc* procedure of averaging over a suitably chosen ensemble of trajectories is used to obtain a single eigenvalue. Remarkably enough, quantization results were obtained in the chaotic regime, the mean square width of final energies in the ensemble being quite large in that case.[12a] Various problems, reported in Ref. 12 for resonance systems, may or may not require special manipulation.

Several perturbation methods have also been used to calculate semiclassical eigenvalues for resonance systems. Such methods can be very effective. While the algebra for each method can become very complicated (for the higher states one needs to use high order perturbation theory), symbolic manipulation programs have been very useful for that purpose. The limitations of perturbation theory lie in the evaluation of the expressions (when H is complicated) and in the approximation of perturbation theory itself (small divisors problem). Birkoff–Gustavson perturbation theory with eighth degree normal form has been used with good results for the calculation of primitive semiclassical[6] and uniform semiclassical (USC) eigenvalues[7] for a 2D 1:1 resonance system. In the USC case certain splittings of degeneracies were obtained. Implementation for the USC required the use of curvilinear coordinates (polar coordinates[3]) appropriate to the shape of the "trajectory." In the primitive SC case, topologically appropriate (curvilinear) quantization paths were employed.

Another perturbation method, the method of "averaging," has been used in second order to treat low lying states in a 2D 2:1 resonance, with good results.[33a] We have used it for low lying states for other resonant systems, again with good results.[33b] (For higher states a higher order would be needed.) Since the method employs annihilation–creation operators, it is not semiclassical in the strict sense. An analogous method, the "algebraic quantization" method, is based on Birkoff–Gustavson perturbation theory plus annihilation–creation operators and has been used (with a fourth degree normal form) with good results for the low lying states of a 2D 1:1 resonance system.[34]

We have used a low order perturbation theory to obtain a functional form for designing a USC approximation[15] in an avoided crossing problem. The latter arose from a 3:1 resonance.[14] Trajectories were then used to calculate the canonical invariants (phase integrals) contained therein[15] and to calculate the eigenvalue splittings.

In some respects, trajectory and perturbation methods are complimentary, as already noted. The perturbation method can be very effectively used to treat low lying states or, when it does not break down in the higher orders, the higher states, when the potential energy is simple enough for ready evaluation of the expressions, or for being expressed in terms of annihilation–creation operators.

Trajectory methods, on the other hand, can be equally used to low and high states, and for simple and complicated potential, provided the trajectories themselves are quasiperiodic. This quasiperiodicity can pose a serious limitation to trajectory methods (apart from some cases treated by AS[12(a),12(c)] using ensembles). In one case, for example, a perturbation method for a 1:1 resonance was useful even in a regime where classical chaos occurred.[6,7] Presumably it could be so used because (as in perturbation theory) the underlying quantum spacings of sequences were "regular,"[35] the classical chaos apparently being on a scale too small compared with h to affect the quantum mechanics.[36]

We summarize next some of the merits and limitations of the present trajectory-close method.

One of its attractive features is its simplicity—it does not break down or become *ad hoc* when resonances occur, does not involve the use of curvilinear coordinates for resonance systems, nor employ perturbative techniques, a window technique, or a perturbation to off-resonance. Also absent is the need for interpreting the sometimes complicated spectra which can ocur in resonance systems or for averaging over an ensemble of trajectories. The method is "exact" within primitive semiclassical (EBK) approximation. It is easily programmed and requires little computer time. In particular, with the recent developments described earlier,[17,24] it is roughly estimated to require about two orders of magnitude less computer time than AS for a 2D system and one order of magnitude less for 3D when, as in resonance systems, AS must be ensemble averaged. (Direct comparisons would be needed to obtain more reliable estimates.)

The present method has several limitations, three of which it shares with the other trajectory methods (the ensemble-averaged AS appears to suffer less from the first of these): The trajectories should be quasiperiodic. In the case of trajectories whose shapes are sufficiently distorted by the resonance, some knowledge of that shape is also needed.[37] (Methods are available for determining the shapes of 3D trajectories.[20,38]) Finally, a USC supplementary method is required for trajectories which are near separatrices, as in the $l = 0$ and $K = 0$ states referred to earlier. The trajectory-close method itself is limited in the number of coordinates that it can now conveniently treat (3 or perhaps 4). In principle, at least, the other methods are more readily adapted to

the many-coordinate case, though as judged by recently published results described earlier the reliability of each remains to be established in individual cases.

One very recent development is the use of local potential functions calculated from a grid of *ab initio* points.[39] These functions can be used directly in trajectory calculations and, with no extra difficulty, the present trajectory-close method can be used to obtain semiclassical eigenvalues. It is not clear how the adiabatic switching method could be used in this case.

Other more quantum mechanical methods, such as wave packet[40] (apart from the citation to Ref. 10), path integral,[41] or other quantum methods lie outside the scope of the present survey and have not been considered here. In any event there have been relatively few accurate comparisons with exact eigenvalues for resonance systems. Nor have we discussed here methods which have been used to determine semiclassical wave functions in resonant systems.[42] The use of the more coarse-grained methods is expected to become particularly important in more complicated systems where individual eigenvalues and spectral lines may give more information than can profitably be used.

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